

Illinois Central College

CHEMISTRY 130

Laboratory Section: _____

Name: _____

Valence Bond Theory: Hybridization

Objectives

To illustrate the distribution of electrons and rearrangement of orbitals in covalent bonding.

Background

Hybridization:

In the formation of covalent bonds, electron orbitals overlap in order to form "molecular" orbitals, that is, those that contain the shared electrons that make up a covalent bond. Although the idea of orbital overlap allows us to understand the formation of covalent bonds, it is not always simple to apply this idea to polyatomic molecules. The observed geometries of polyatomic molecules implies that the original "atomic orbitals" on each of the atoms actually change their shape, or "hybridize" during the formation of covalent bonds.

But before we can look at how the orbitals actually "reshape" themselves in order to form stable covalent bonds, we must look at the two mechanisms by which orbitals can overlap.

Sigma and Pi bonding

Two orbitals can overlap in such a way that the highest electron "traffic" is directly between the two nuclei involved; in other words, "head-on". This head-on overlap of orbitals is referred to as a **sigma bond**. Examples include the overlap of two "dumbbell" shaped "p" orbitals (Fig.1) or the overlap of a "p" orbital and a spherical "s" orbital (Fig. 2). In each case, the highest region of electron density lies along the "internuclear axis", that is, the line connecting the two nuclei.

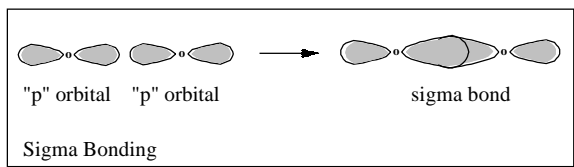


Figure 1.

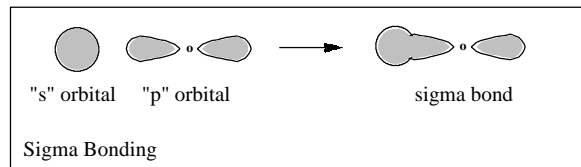


Figure 2.

On the other hand, when "p" orbitals on adjacent atoms are oriented parallel to one another, a "side-to-side" overlap of orbitals is possible (Fig. 3). This type of sideways overlap can only be accomplished by "intact" (that is, unhybridized) "p" orbitals and is referred to as Pi bonding. In the case of Pi bonds, the highest electron traffic lies above and below the internuclear axis.

NOTE: The "first" bond to form between two atoms is of the Sigma type (above). Whenever multiple bonds (such as double or triple) are present between two atoms, one is always a Sigma and the remaining bond(s) is(are) of the Pi type.

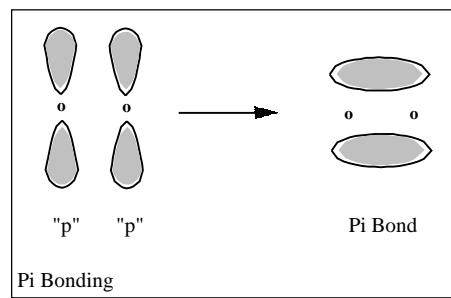


Figure 3.

When an atom involves itself in the process of forming covalent bonds, it is most often the case that orbitals reshape (or hybridize) themselves in order to provide more stable orbital overlap.

For example, in the compound CCl_4 , the carbon atom uses its 2s orbital and all three of its 2p orbitals to provide four bonding sites for the four chlorine atoms. However, examination of the bonds in CCl_4 reveals that all four bonds appear to be identical even though totally different atomic orbitals were used. This would imply that some "hybridization" of the orbitals has occurred.

Quantum mechanical models of the possible shape of the hybrid orbitals in CCl_4 reveal four identical dumbbell shaped orbitals (where one end of the lobe is smaller) arranged in perfect tetrahedron. (Fig.4) This is consistent with the Valence Shell Electron Pair Repulsion Theory which states that the four bonds in CCl_4 would arrange themselves as far apart as possible.

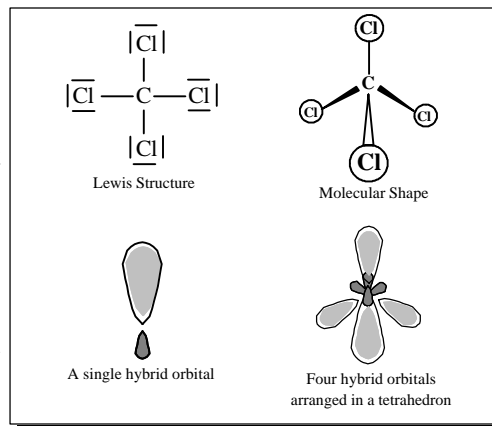


Figure 4.

Note that since the "hybridized" orbital is no longer an "intact" p orbital (since the "s" orbital has been thrown into the melting pot) **it is not capable of forming Pi bonds**. Hybridized orbitals have only two functions; (1) to form sigma bonds and (2) to provide housing for lone pairs.

Therefore, it is a simple task to determine the number of required hybrid orbitals by looking at the Lewis Structure and counting the number of peripheral atoms (which must have one sigma bond each) and the number of lone pairs on the central atom. Each of these requires one hybrid orbital.

The following models illustrate five ways atomic orbitals can hybridize into reshaped molecular orbitals and how the arrangements of these bonding orbitals is consistent with VSEPR Theory.

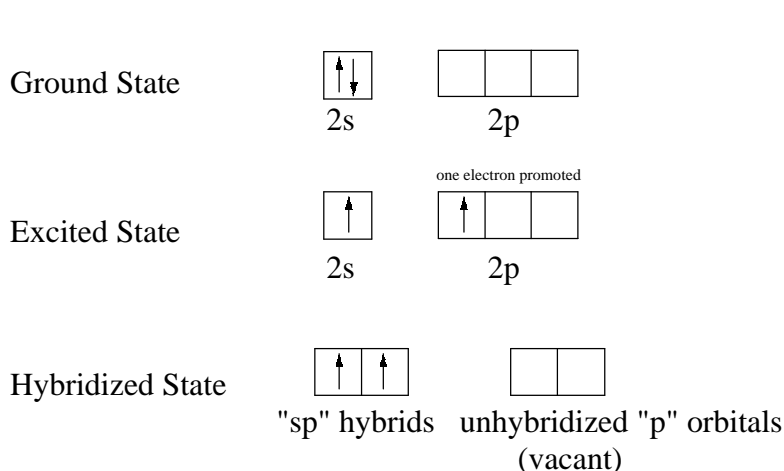
In a later section, the formation of Pi bonds using unhybridized p orbitals is discussed.

sp hybridization (2 hybrid orbitals)

Looking at the orbital diagram for the valence shell of Beryllium in BeCl_2 , it shows a pair of electrons in the 2s subshell. However, in order for Be to form two covalent bonds (see Lewis Structure, below), it clearly must have two **single** electrons in each of two orbitals. We theorize then, that an electron is "promoted" just prior to bonding into the 2p subshell.

Although this "promotion" does explain how Beryllium could form two bonds, it doesn't explain why the bonds appear to be identical when examined. Since the bonds were seemingly constructed using an "s" orbital and a "p" orbital, they should be different...yet they are not. The theory of "hybridization" implies that the two orbitals involved actually "melt" into two equivalent "hybrid" orbitals of identical shape and size. These "hybrid" orbitals are responsible for the two sigma bonds in BeCl_2 and are referred to as the "sp" hybrids.

The orbital diagrams below show the "**ground state**" before bonding, the "**excited state**" where the 2s electron has been promoted to the 2p, and the "**hybridized state**" where the two single electrons now reside in equivalent orbitals. Note that any left-over "p" orbitals are referred to as "unhybridized orbitals". These unhybridized orbitals are used to form any double or triple (Pi) bonds in a molecule and *since this structure shows no multiple bonding, these unhybridized orbitals are vacant*. It should be noted that the "sp" hybrid orbitals will arrange themselves in a **linear geometry**.

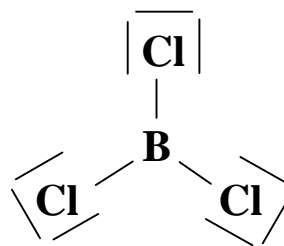
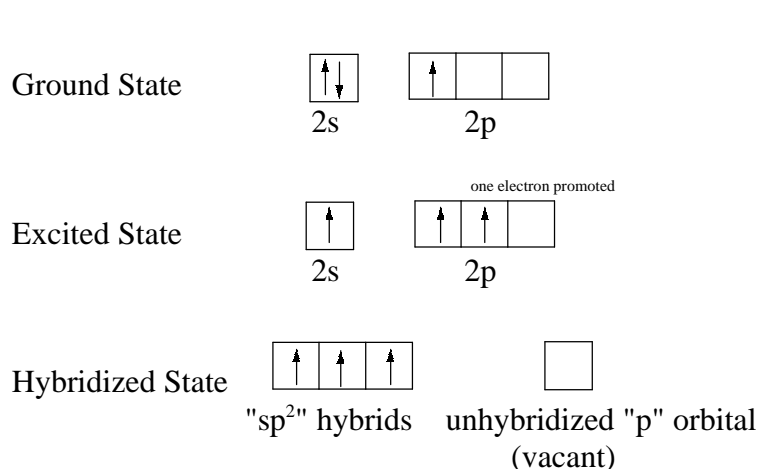


sp² Hybridization (3 hybrid orbitals)

Looking at the orbital diagram for Boron in BCl_3 , we see three valence electrons....two in the 2s subshell and one in the 2p. But again, in order for Boron to form three covalent bonds as seen in its Lewis Structure, it must provide three **single** electrons in three separate orbitals. The promotion of an electron to the 2p subshell just prior to bonding is represented below as the "excited" state of the Boron as it begins to bond.

Since examination of the sigma bonds in BCl_3 reveals that they too are identical, it is assumed that hybridization of the s orbital and two of the p orbitals occurs providing three hybrids of identical shape, size and energy.

It should be noted that these three " sp^2 " hybrids would arrange themselves as far apart as possible forming a **trigonal planar electron arrangement**.

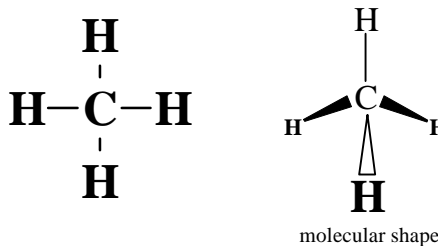
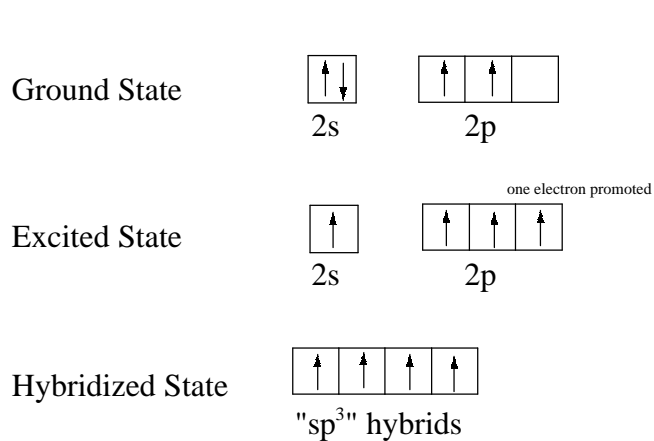


Boron needs only three hybrid orbitals in order to form the three sigma bonds with the chlorines.

sp^3 hybridization (4 hybrid orbitals)

In the case of methane CH_4 , the ground state of carbon reveals a pair of electrons in the 2s and two single electrons in the 2p. This is not consistent with the need for four single electrons required to form the four bonds with the hydrogens, so again, electrons are promoted into the p subshell just prior to bonding.

These four atomic orbitals (the s orbital and all three p orbitals) apparently hybridize into four equivalent molecular orbitals referred to as the sp^3 hybrids. These four orbitals arrange themselves in a **tetrahedral geometry** in order to minimize repulsion effects.



Carbon needs four hybrid orbitals in order to form the four sigma bonds with the hydrogens. In order to form four hybrids, it must use all four of its available valence shell atomic orbitals.

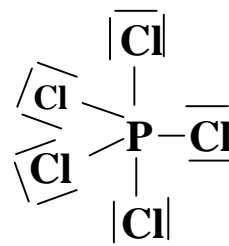
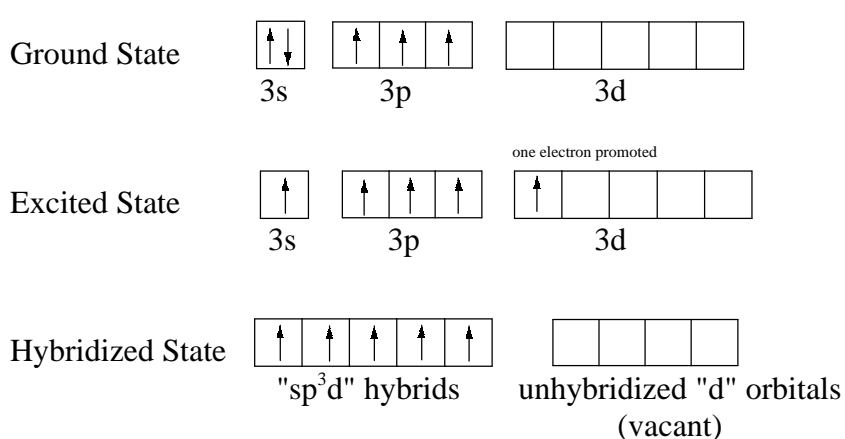
Expanded Octets

sp^3d hybridization (5 hybrid orbitals)

In order to have an expanded octet, the central atom of the molecule must have at least three shells of electrons in order to accommodate more than eight electrons in its valence shell. It isn't until we reach the third main shell that the "d" sublevel exists to provide enough orbitals for an expanded octet.

For example, PCl_5 , has a ground state showing two electrons in the 3s sublevel and three single electrons in the 3p sublevel. Note that there is a vacant 3d sublevel available for the promotion of electrons. The promotion of electrons that occurs just prior to bonding in PCl_5 provides five single electrons for the five P-Cl bonds, but requires the use of one of the "d" orbitals to do so.

Once the electrons are promoted, hybridization of the s orbital, three p orbitals and one d orbital into five equivalent molecular orbitals gives us the sp^3d hybrids responsible for the bonding in PCl_5 . These five hybrid orbitals will adopt a **trigonal bipyramidal geometry** in order to get as far from each other as possible.

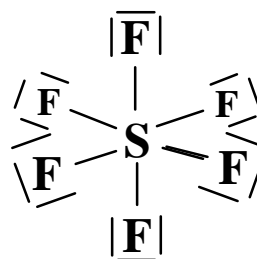
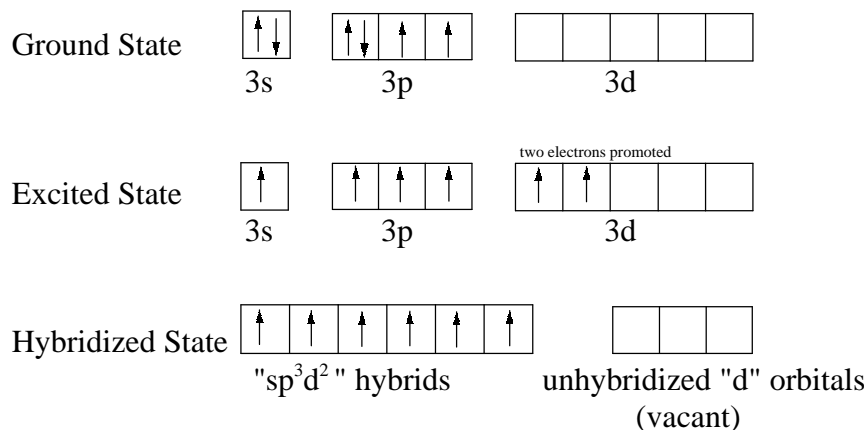


Phosphorus must provide five hybrid orbitals to form the five sigma bonds seen in its Lewis Structure. This requires the use of one of its "d" orbitals.

sp^3d^2 hybridization (6 hybrid orbitals)

An examination of the ground state of sulfur in SF_6 reveals a pair of electrons in the 3s, a pair and two single electrons in the 3p and a vacant 3d sublevel. It is presumed that just prior to bonding, promotion of the electrons occurs in such a way as to provide the six single electrons necessary to provide the six bonding sites for the fluorines. So, the "Excited" state shows that the electrons promoted will reside in the first two available "d" orbitals.

These six occupied atomic orbitals apparently hybridize into six equivalent molecular orbitals known as the sp^3d^2 hybrids. These six hybrid orbitals will arrange themselves in an **octahedral geometry consistent with the VSEPR Theory discussed in last week's lab.**



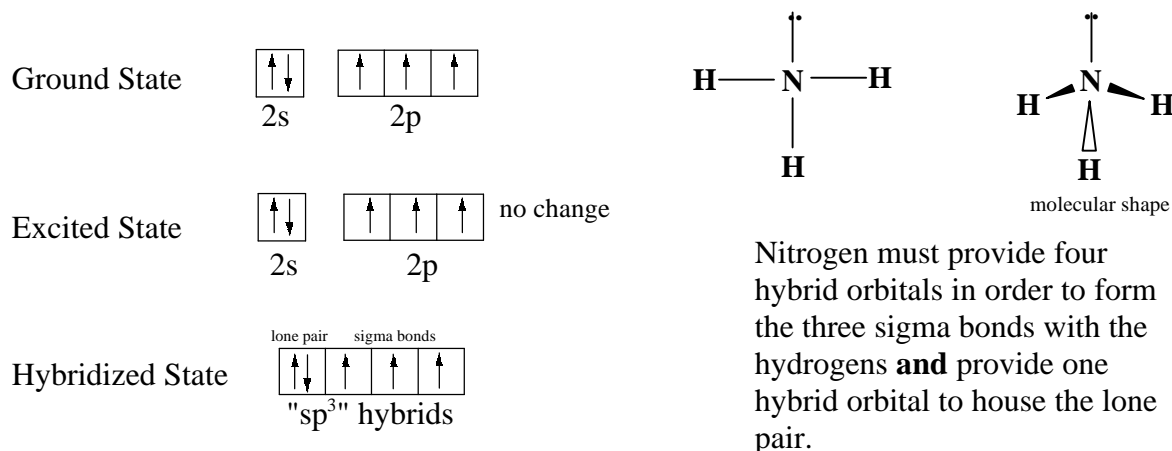
Sulfur must provide six hybrid orbitals to form its six sigma bonds with the fluorines.

Treatment of Lone Pairs on the Central Atom

As mentioned earlier, the hybrid orbitals in a molecule basically have **two** responsibilities; (1) to form the first bond between two atoms and (2) to house lone pairs. Note: any double or triple (Pi) bonding is handled by the "unhybridized orbitals".

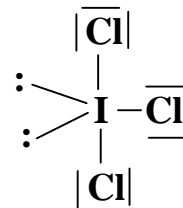
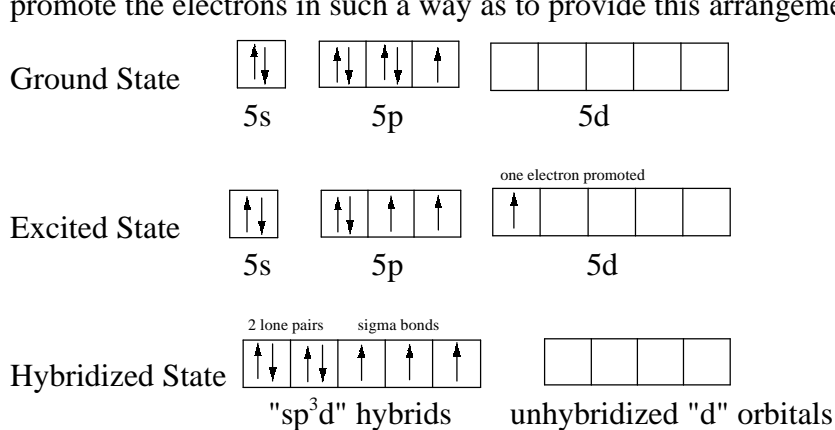
In the case of ammonia NH_3 , we see a ground state with a pair of electrons in the 2s sublevel and three single electrons in the 2p. Since the Lewis Structure of NH_3 shows a lone pair on the nitrogen (which resides in one of the hybrid orbitals), the orbital diagram should likewise show a pair of electrons (representing the lone pair) and three single electrons to provide the three bonding sites for the three hydrogens. So, you will note that no promotion of electrons is required here for the excited state as the existing arrangement is just what we need.

These atomic orbitals do hybridize however, into four equivalent sp^3 hybrids with one containing the lone pair and the other three containing the single electrons used to bond with the hydrogens.



In essence, what we have done is to make the orbital diagrams match what we see in the Lewis Structure.

For example, let us look at the Lewis Structure of ICl_3 . The picture shows that the Iodine has 2 lone pairs and three bonds meaning that Iodine must hybridize in such a way as to provide five hybrid orbitals (that is, sp^3d). These five hybrid orbitals will contain two pairs, representing the lone pairs in the Lewis Structure, and three single electrons representing the three bonding orbitals for the chlorines. We must make certain that when we write out the excited state, we promote the electrons in such a way as to provide this arrangement.



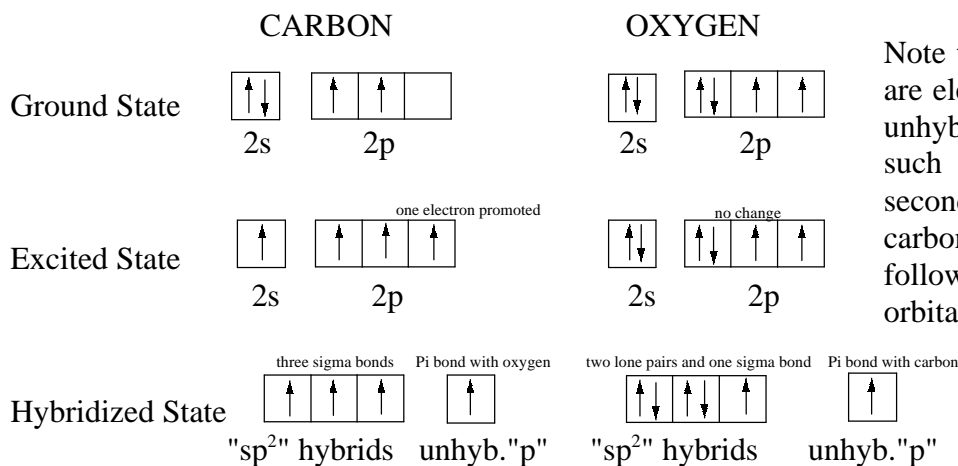
Iodine must provide five hybrid orbitals to form the three sigma bonds with the chlorine **and** provide two hybrids to house its two lone pairs.

Multiple Bonding. (Pi bonding using Unhybridized p orbitals)

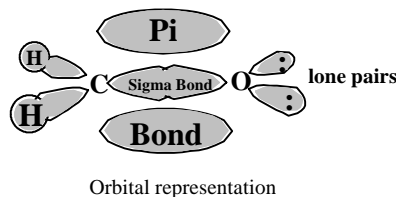
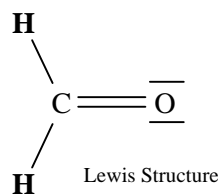
As mentioned previously, the unused, or unhybridized orbitals handle any multiple bonding that occurs, so if you draw a Lewis Structure that contains double or triple bonds, you can be certain that there are electrons residing in those unhybridized orbitals.

For example, formaldehyde H_2CO . The Lewis Structure (See top of p.8) shows that carbon must use its "s" orbital two of its "p" orbitals to "melt" into three equivalent sp^2 hybrids, each of which will contain a single electron. This leaves one electron left over in **an unhybridized "p" orbital** to form the second bond (the Pi bond) with the oxygen.

If we apply the same hybridization model to the oxygen involved, it must also provide three hybrid orbitals. That is, one for the sigma bond formed with the carbon and two to house its lone pairs. This would be consistent with its electron arrangement allowing an electron to reside in a **left-over unhybridized p orbital**. The unhybridized p orbitals on the carbon and the oxygen could be oriented in the same plane allowing a side-to-side overlap thus forming the **second** (Pi) bond between them.



Note that in this case, there are electrons residing in the unhybridized "p" orbitals in such a way as to form a second bond between the carbon and the oxygen following the "Pi" model of orbital overlap.



So, by looking at the Lewis Structure, and determining the "orbital needs" to match the picture, we can show a hybridization model that is consistent with the Structure itself.

Summary

The following table summarizes the five types of hybridization addressed in this exercise.

Number of required hybrid orbitals	Electron Pair Arrangement	Type of Hybridization	Atomic Orbitals used to create Hybrids
2	Linear	sp	one s, one p
3	Trigonal planar	sp ²	one s, two p's
4	Tetrahedral	sp ³	one s, three p's
5	Trigonal bipyramidal	sp ³ d	one s, three p's, one d
6	Octahedral	sp ³ d ²	one s, three p's, two d's

Procedure.

1. Draw the Lewis Structures and construct the models for the molecules listed on the report sheet. Have your instructor check the models before proceeding.
2. To determine the type of hybridization, simply count the number of peripheral atoms **plus** the number of lone pairs on the central atom to determine the number of hybrid orbitals required according to your Lewis Structure. Remember to use vacant bonding pegs to represent lone pairs on the central atom.
3. Refer to the hybridization schemes listed in the lab text to construct the orbital diagrams for each of the compounds. The orbital diagrams are for **the central atom only**.
4. Answer the remaining questions concerning the number and type of bonds, molecular shape, etc.

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REPORT SHEET: Valence Bond Theory: Hybridization

	<u>C</u> F ₄	<u>P</u> F ₃	<u>C</u> lF ₃
Lewis Structure			
Number of sigma bonds on central atom			
Number of lone pairs on central atom			
Hybridization type (sp, sp ² , sp ³ etc.)			
Ground State distribution of valence electrons			
Excited State distribution of valence electrons			
Hybridized State distribution of valence electrons			
Electron Pair Arrangement			
Molecular Shape			
Bond angle(s)			
Are the individual bonds polar?			
Is the molecule polar?			

	<u>Xe</u> F ₄	<u>I</u> Br ₅	<u>C</u> OCl ₂
Lewis Structure			
Number of sigma bonds on central atom			
Number of lone pairs on central atom			
Hybridization type (sp, sp ² , sp ³ etc.)			
Ground State distribution of valence electrons			
Excited State distribution of valence electrons			
Hybridized State distribution of valence electrons			
Electron Pair Arrangement			
Molecular Shape			
Bond angle(s)			
Are the individual bonds polar?			
Is the molecule polar?			

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PRELAB: Exp.13 Valence Bond Theory

For the molecule AsCl_5 , perform the following operations.

1. Draw the correct **Lewis Structure**.

2. How many **sigma bonds** does the Arsenic form? _____

How many **lone pairs** does Arsenic have? _____

What **type of Hybridization** does Arsenic exhibit in this molecule based on the number of hybrid orbitals required? (sp , sp^2 , sp^3 , etc.) _____

3. Show the **Ground State** distribution of the valence electrons on Arsenic.

4. Show the **Excited State** distribution of valence electrons on Arsenic.

5. Show the **Hybridized State** distribution of the valence electrons on Arsenic.

6. What is the **molecular shape** of the molecule?

